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LEACHING BEHAVIOR OF MICROTEKTITE GLASS
COMPOSITIONS IN SEA WATER AND THE EFFECT
OF PRECIPITATION ON GLASS LEACHING

INTRODUCTION

Microtektites associated with the North American strewn field (age= 3.4×10^7 years), the Ivory Coast strewn field (age= 1.0×10^6 years), and the Australasian strewn field (age= 7.2×10^5 years) have been found in abundance in deep-sea sediments.¹⁻⁴ Despite their great age and their relatively low silica content (usually 60-70%, in some cases as low as 50%)^{4,5} these glasses have survived largely intact. The maximum observed extent of corrosion⁶ does not exceed 90 μm and the hydration thickness⁷ is smaller than 20 μm . In general, the corrosion and hydration thicknesses are smaller than 5 μm and 2 μm , respectively.

In recent years, accumulation of leach data on numerous glass compositions has led to the conclusion that corrosion rates vary systematically with composition. In particular, Plodinec, Jantzen and Wicks,⁸ following Paul's approach,⁹ were able to establish a correlation between glass dissolution rates and glass composition on the basis of the free energy of hydration of the glass constituents. The leach rates of various man-made ancient, medieval, and modern glasses (including nuclear waste glasses) as well as those of natural glasses such as land tektites, obsidians, basalts, and Libyan desert glass, were shown to follow this general dependence.⁸ In the case of land tektites, the

observed extent of corrosion in nature was shown to be in close agreement with the results of laboratory tests.¹⁰ In the case of silicate glasses which contain roughly similar proportions of mono-, di- and tri-valent oxides, to one another, a primary factor in determining corrosion rates is the silica content of the glass. For instance, the leach rates of high-silica glasses (95-100% SiO₂) were found to be lower by approximately one order of magnitude than those of tektites, 8-10 obsidians and Pyrex borosilicate glasses,⁸ which contain approximately 75-80% SiO₂. The corrosion rates of the latter glasses are, in turn, lower by another order of magnitude than those of glasses such as Savannah River Laboratory SRL-165 (a nuclear waste glass) and basalt glass, which contain approximately 50% SiO₂. Low-silica Australasian microtektites of the bottle-green type belong, on the basis of their silica content, to the latter class of glasses. Given the rate of mass loss from such glasses (approximately 2×10^{-2} g.m⁻².d⁻¹, at 90°C, see Ref.8), a density of approximately 2.8 g.mL⁻¹,⁵ and an activation energy of dissolution of approximately 80 J.mol⁻¹ (characteristic of land tektites¹⁰ and of silicate glasses in general,¹¹) the expected rate of microtektite dissolution at an ocean floor temperature of 2°C can be calculated to be approximately 6×10^{-6} mm.yr⁻¹. This result is much higher than the rates cited above,⁶ and since dissolution at this rate would have resulted in the complete disappearance of microtektites (which typically have diameters of 0.1-0.2 mm, at most 0.5 mm)⁵ it can be concluded that actual

corrosion has proceeded much more slowly, or, in other words,⁶ for a much shorter equivalent period of time than the actual age of the microtektites.

One possible reason for the slow rate of dissolution of microtektites in nature is the composition of the leachant to which they have been exposed. The tests used to determine the leach rates cited above (see Refs. 8,10,11) were carried out using de-ionized water as the leachant and under conditions of high dilution and short contact time between the sample and a given volume of water, minimizing the accumulation of solutes in the water. This is appropriate, for instance, for purposes of comparison with field data in the case of the corrosion of land tektites exposed to rain water. On the other hand, under natural conditions microtektites are in contact with the interstitial pore water of the sea-bed sediments. This water has a large amount of solutes, since it is similar in major element composition to sea-water and is furthermore enriched with respect to the principal constituents of the sediments, most notably silica.

In the present study it was attempted to account for the slow corrosion rates of microtektite glass in nature by comparing the leach rates of synthetic microtektite glass samples in de-ionized water and in sea-water, respectively. In order to obtain systematic data about leachant composition effects, leach tests

were also carried out with synthetic leachant compositions enriched with respect to silica or depleted with respect to certain major components of sea-water (Mg, Ca).

EXPERIMENTAL

Glass Preparation

The glass composition prepared for the leach studies is based on simulation studies of bottle-green Australasian microtektites carried out at Rutgers University¹². This composition is the base glass described in Table I. It is very difficult to follow the dissolution of this glass in sea-water and in related leachants because most of its components, in particular the more soluble ones such as Na, K, Ca and Mg, are present at high levels in sea-water. Accordingly, a doped glass was prepared, with Cs substituted for the potassium present in the base composition, Sr substituted for 1/2 of the amount of Ca, and 0.5% B₂O₃ added to the overall glass composition. (The latter was introduced as boric acid). In this way it was intended to use Cs as an indicator for the leaching of the monovalent cations, Sr as a representative of the divalent cations, and boron as a representative of the glass formers. Cs, Sr, and, in particular, boron are useful in establishing upper limits on the leach rates of glasses because of their high solubility in neutral aqueous media.¹³ The target compositions of the base glass and the doped glass, respectively, as well as an actual analysis of the doped glass, are given in Table I. The glass was analyzed by

dissolving powdered specimens in a 1:1 mixture of concentrated HF and HCl at a temperature of 90°C for 1 hour.

The glasses were prepared by mixing together powdered oxides of Si, Ti, Al and Fe (Fe_3O_4 was used in the case of Fe) and powdered carbonates of Mg, Ca, Na, Sr and Ba. The mixed powders were heated under vacuum to a temperature of 1000°C at a heating rate of 200°C/hr. A mixture of 5% H_2 in N_2 was introduced and the temperature was raised from 1000°C to 1400°C at a rate of 100-200°C/hr. The temperature was held at 1400°C for 1 hr. The melt was allowed to cool down to room temperature at a rate of approximately 100°C/hr under the N_2 - H_2 atmosphere. Melting was carried out in a fused silica crucible with a graphite liner. The heating elements used in the furnace were made out of molybdenum wire.

Leach Test Procedures

Samples of the doped glass were crushed and the -40+60 mesh fraction of the powder was separated out for leaching studies. Several sets of leach tests were carried out, each set in a different leachant. In each set 4 leach vessels were used, two of which contained 0.6 g of glass powder and 20 mL of leachant each. This amount of glass powder corresponds to a surface area of approximately $5.8 \times 10^3 \text{ m}^2$,¹⁴ and the resulting surface-to-volume (S/V) ratio is 293 m^{-1} . A low S/V ratio is desirable in studying leachant composition effects to minimize the consequences of the accumulation of glass leaching products in the aqueous phase.¹⁴ However, excessively high dilution would lead

to problems in analyzing the levels of leached glass components. Each of the other two vessels in each set contained only 20 mL of leachant to serve as a blank. The leach vessels were 60-mL PFA polytetrafluoroethylene containers. They were placed in an environmental chamber at a temperature of $(90 \pm 1)^\circ\text{C}$. The entire volume of the aqueous phase was removed for analysis and replaced by fresh leachant at certain intervals. These intervals were 1-day long during the first week of testing, 7-day long during the next 12 weeks, and 28-day long thereafter.^{15,16}

The pH of the leachates was measured using a Ross-type combination glass electrode after rapid cooling to room temperature. The concentrations of Si, Ti, B, Ca, Fe, Al, Sr, and K were measured using DC plasma spectrometry, Mg by atomic absorption, Cs by flame emission, and Na both by DC plasma spectrometry and atomic absorption. In the cases of leachants which contain high levels of certain elements, e.g. Na, K, Mg and Ca in seawater, these elements were omitted from the analysis. No attempt was made to filter the solutions prior to analysis. Except in the case of one set (SW+Si,Al, see below), all leachates and leachant blank solutions were clear and transparent.

Normalized leach rates, L_i , for component i of the glass during the n -th interval of exposure to the leachant were calculated using the expression¹⁷ $L_i = (C_i - C_i^*) / f_i \cdot Dt_n \cdot (S/V)$, where C_i is the average concentration of i in the two leachates, C_i^* is the average concentration in the two blanks, f_i is the abundance of i in the glass, Dt_n is the duration of the n -th leaching

interval, and S/V is the ratio of the surface of the glass (see Ref. 14 for evaluation of S in the case of powders) to the volume of leachant to which the glass is exposed.

Leachant Compositions

The compositions of the leachants used in this study are detailed in Table II. De-ionized water (DIW) was the reference leachant. Pacific Ocean sea-water (POSW) was obtained from Scripps Institution of Oceanography, University of California, San Diego. Simulated sea-water (SW) was prepared according to Furon,¹⁸ based on studies by Lyman and Fleming¹⁹ and by Kalle²⁰. All salts listed in Table II were of Analytical Reagent Grade and dissolved in de-ionized water. Since the average content of silica in sea corresponds to 3 mg/L Si,²¹ a corresponding amount of sodium silicate was included in the simulated sea-water composition. The levels of silica in the interstitial pore water of the seabed sediments are considerably higher, typically around 15-30 mg/L Si.²² Accordingly, a solution simulating this composition was prepared using the same formulation of the major elements in sea-water with the addition of an amount of sodium silicate corresponding to 20 mg/L Si. No quantitative data are available for the alumina content of interstitial pore water. Since this water is present in intimate contact with alumina silicates in the sediment, an amount of sodium aluminate corresponding to 0.7 mg/L Al was also added to this composition. The resulting leachant is designated in Table II as SW+Si,Al.

In order to study the effect of the presence of individual elements in the sea-water composition on the leach behavior of glasses, leachants depleted with respect to certain elements were prepared. These leachants included simulated sea water prepared without introducing Mg^{2+} while adding sufficient NaCl to give the same ionic strength as in SW. The Mg-deficient solution was designated SW-Mg. Another solution was prepared with NaCl substituted for both Mg and Ca salts. This solution is SW-Mg,Ca. These two leachants had the same silica content (3 mg/L Si) as SW. Finally, in order to highlight the role of high Si levels in leachants such as interstitial pore water, a solution of sodium silicate in de-ionized water corresponding to a concentration of 50 mg/L Si was prepared. This solution is DIW+Si. In order to complete the study with respect to the effects of pH, especially in the case of the divalent metals (see below), tests were also carried out in a pH3 buffer solution (0.05 M potassium phthalate - HCl). This solution is called pH3 in Table II. All the leachants were stored in polyethylene containers at room temperature. Both appearance and chemical composition remained unchanged for at least 6 months, except in the case of SW+Si,Al, which became turbid (see below).

RESULTS

As usual in the case of glass leaching, the leach rates of the various glass components during the first few days of the tests were high and they dropped off as the tests progressed, finally approaching constant values. The leach rates based on Si

for the microtektite glass composition in synthetic sea-water without Mg (SW-Mg) are shown in Fig.1 as a function of total exposure time (measured up to the middle of the most recent leaching interval).

Actual sea-water contains significant background concentrations of all the elements which are monitored for leaching out of the glass. This is true even in the cases of minor elements such as boron and Sr, which are present in sea-water at levels of 5 mg/L and 8 mg/L, respectively.²¹ Similarly, significant amounts of such elements can be detected in the simulated sea-water leachants because of the high solute concentrations and the presence of persistent traces of impurities (e.g., Sr and Al in the Ca salts). Accordingly, both detailed results of leachate concentrations and net leach rates are given in the next two Tables. Table III represents the results of both blank and leachate analysis at the end of 10 weeks of leaching at 1-week intervals (except during the first week, when the leachate was changed at 1-day intervals). At this point the 1-week leachate concentrations (and, consequently, the leach rates) were observed to have become independent of time. Table IV represents the results at the end of 17 weeks of leaching, after the leaching intervals were extended to 4 weeks. In each triplet of lines in Tables III and IV the upper figures (C*) represent the average blank concentrations, the middle figures (C) represent the average leachate concentrations, and the lower figures (L) represent normalized leach rates.

DISCUSSION

1. Leaching Kinetics of Glass Constituents

Two general phenomena observed in the leaching of multicomponent silicate glasses (in particular compositions used in nuclear waste vitrification) are a change in leach rates with exposure time and differences among the normalized leach rates of the various glass components.^{13,17} Leach rates usually decrease with time (except in cases where initial leaching causes a major pH rise), and eventually level off at near-constant values. Comparisons of the normalized leach rates of various glass components indicate that highly soluble species, such as the light alkalis (Na, Li) and boron, exhibit the largest extent of dissolution, while glass components which are scarcely soluble in aqueous media at the pH range of interest (e.g. Fe, Mn, Ni, Ti, Zr at near-neutral or weakly basic pH) exhibit the smallest leach rates (normalized on the basis of their abundance in the glass composition). Other components of the glass are intermediate in character. These include Si, Al, heavy alkalis (e.g. Cs) and alkaline earths. The relative leach rates of such components are highly dependent on the exact composition of the surrounding aqueous media. For instance, in very dilute solutions the normalized leach rates of Si, Al and Cs can approach those of the most leachable species such as Na or B, but the presence of relatively low levels of Si (typically of the order of 10 mg/L) causes major decreases in both the relative leach rates of Si, Al, Cs, etc. and in the absolute leach rates of the glass as a

whole. Leach rates of the alkaline earths in the near-neutral and weakly basic pH range are extremely dependent on pH, and they follow the order of oxide or hydroxide solubility, i.e. $Ba > Sr > Ca > Mg$. At pH 6-6.5, for instance, the observed leach rates of Sr are generally similar to those of Na and B, while at pH 9.5-10 Sr is one of the least leachable glass components. In more acidic environments other oxides become soluble and the leach rates of the corresponding glass components (e.g. Al, followed by Fe and Ti) sharply increase. This gives rise, for instance, to the high rates of aluminosilicate glass dissolution at low pH.^{23,24} The difference in leach rates among the various glass components can result in the formation of an alteration layer, enriched with respect to the less soluble species, on the glass surface. The initial change in leach rates with time reflects the time required for build-up of the layer until its composition and structure become nearly constant.^{13,17}

The results of present studies on glasses of the microtektite composition are generally in agreement with these findings both in terms of the dependence of leach rates on time (see Fig.1) and in terms of variations among elemental leach rates (see Tables III and IV). The presence of thin altered layers depleted with respect to Na and K ($\sim 0.02\mu m$) on the surface of land tektites exposed to water was inferred from solution chemistry studies¹⁰ and directly confirmed by SIMS analysis.²⁵ In the case of microtektites, surface layers depleted with respect to Na, Ca and Mg, but not with respect to Si, Al and K, were

found to extend for ranges of up to 2 μm , and in rare cases of up to 20 μm .⁷ While present experiments in sea-water could not be used to measure the dissolution rates of Na, K, Ca and Mg because of the high levels of these elements in the leachant composition, the results obtained in de-ionized water and in synthetic sea-water depleted in Mg+Ca or in Mg alone clearly indicate that some elements leach out faster than others. For instance, Fe and Ti consistently exhibit low leach rates compared with other glass components.

Unfortunately, the use of dopants (Sr, Cs, B) had limited applicability in monitoring the leaching kinetics in leachants based on sea-water. These species were observed to leach out much faster than any of the other glass components. The high leach rates observed for Cs and for Sr in leachants based on sea-water can be attributed to specific exchange of K^+ , present at high levels in sea-water, for the chemically similar Ca^+ ion of the glass, and to a similar displacement of Sr^{2+} by Ca^{2+} .²⁶ However, the measurements of dopant leach rates was very useful in comparing the leach rates in de-ionized water with those observed in a pH3 buffer solution and in silicate water (see Tables III and IV).

2. Effects of Leachant Composition on Leaching Kinetics

The data in Tables III and IV show that the leach rates measured with a leaching period of 28 days are generally lower by a factor of approximately 2 compared with the results obtained with a leaching period of 7 days. This finding is again in

agreement with observations on nuclear waste glasses.^{13,17,26} The decrease in leach rates with increased contact time can be attributed to higher concentrations of dissolved glass components in the aqueous phase, enhanced saturation effects and consequent enrichment of the residual glass surface with respect to saturating species such as Si and Al. Accordingly, the leach rates obtained with the shorter leaching interval more accurately reflect the effects of the original leachant composition. In any case, the variations among leach rates in different leachants at the two leaching intervals are very similar.

The dependence of leach rates on leachant composition shown in Tables III and IV can be summarized in the case of Si, the major glass component, as

pH3 >> SW-Si,Al > DIW >> SW-Mg,Ca > SW-Mg > DIW-Si > SW >> POSW

A generally similar order is observed in the cases of all other original glass components (Al, Fe and Ti as well as Na, Ca and Mg in those leachants in which the latter species can be measured), as well as of boron. Slight differences are noted, e. g. the leach rates of Al and Fe in de-ionized water are lower than those observed in SW-Mg,Ca and in SW-Mg. As mentioned in the previous paragraph, the enhanced leach rates of Ca and Sr in leachants based on sea water do not reflect true glass dissolution rates due to specific ion exchange processes.

The high dissolution rates of all glass components (including Si) at pH 3 are due to the large abundance of oxides which are soluble in moderately acidic media but not in neutral

environments (especially the oxides of Mg, Al and Ca) in the glass composition. The large decrease in leach rates upon addition of high levels of silicate (50 mg/L Si) to water is due to the limited solubility of silica in near-neutral aqueous media.^{13,26} Silica dissolution rates observed in leachants equivalent in ionic strength to sea-water but containing no divalent metal ions are lower by a factor of approximately 3 than those observed in de-ionized water. This is not likely to be due to an ionic strength effect, since the solubility of silica shows only a small decrease in the presence of high concentrations of NaCl.²⁷ The reduction in the extent of silica dissolution can be attributed to the higher concentrations of Al in the saline leachates (SW-Mg,Ca and SW-Mg) compared with the Al levels in the DIW leachates, together with the initial presence of approximately 3 mg/L Si in all the synthetic sea-water leachants used in this study. The enhanced concentrations of Al in the SW-Mg,Ca and SW-Mg leachates may be due to the higher ionic strength of these leachants and to the presence of sulfate, which is known to form complexes with Al^{3+} .^{28,29} The presence of dissolved Al is known to reduce both silica solubility³⁰⁻³³ and silica dissolution rates.³⁴ Dissolved silica levels in sea-water reacted with clays are indeed much lower than the solubility level of amorphous silica.³⁵⁻³⁸

A further decrease in leach rates by a factor of at least 5 is observed when the divalent metals (Ca and Mg) are added to the synthetic leachant. This may be attributed to the low

solubilities of Mg silicates^{38,39} (e.g. sepiolite^{35,40} and palygorskite^{41,42}) in water, which accounts for their formation in silica - sea-water systems.^{35,39} Mg and Ca aluminosilicates can also be formed under these conditions and contribute to the silica solubility control.^{36,38,41} Finally, in actual Pacific Ocean sea-water no silica dissolution from the synthetic microtektites is observed. Silica levels in the aqueous phase slightly decrease in the course of contact with the glass. This indicates that some silica from the solution is sorbed on the surface of the glass, probably because of the large abundance of Al, Mg and Fe on this surface.^{33,43} The leach rates of the other glass components are also extremely low.

3. Leach Behavior of Microtektite Glass in Laboratory Tests and in Nature

As mentioned in the Introduction, the dissolution rate of a glass of the microtektite composition in de-ionized water at 90°C is expected to be $2 \times 10^{-2} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, based on the silica content of the glass (50%) as a primary consideration. The results in Tables III and IV are in very good agreement with this value ($1-3 \times 10^{-2} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, depending on contact time).

However, the extent of corrosion of microtektites in their sub-seabed environments is lower by 2-3 orders of magnitude than expected on the basis of this dissolution rate extrapolated to a temperature of 2°C. This discrepancy can be resolved in view of present findings in de-ionized water and in sea-water respectively. As shown in Tables III and IV, no net dissolution of

silica could be observed upon analysis of the Pacific Ocean sea-water leachant and the corresponding leachates. In the case of the other glass components the leach rates observed in sea-water are very low (up to $0.3 \text{ g.m}^{-2} \cdot \text{d}^{-1}$, except in the case of the Sr and Cs dopants which, as mentioned above, are likely to exhibit enhanced leaching due to specific ion exchange reactions irrelevant to the natural ingredients of microtektites). These rates are lower by at least 2 orders of magnitude than the dissolution rates of the glass in de-ionized water under the same conditions. Accordingly, the following conclusions can be made:

a. The observed dissolution rates of microtektites in laboratory tests agree very well with predicted values based on glass composition when de-ionized water is used as the leachant and with field observations of microtektite corrosion when exposed to contact with sea-water.

b. The dissolution rates of microtektite glass in sea-water are slower than the dissolution rates in de-ionized water by more than 2 orders of magnitude.

c. The ingredients of sea-water which are most responsible for the low reactivity towards the microtektite glasses appear to be Mg and Si. The presence of high levels of Mg reduces the saturation levels of Si to values which approximate the concentrations of Si actually present in the sea-water.

These conclusions are also compatible with the fact that the presence of microtektites has been mostly observed in sea-bed sediments rather than on land areas exposed to rainfall.

4. The Effect of Precipitation on Glass Leaching

The most surprising result observed in the present studies is the high rate of glass dissolution in the SW+Si,Al leachant. As detailed above, this leachant was prepared by adding sodium silicate (at a level of 20 mg/L Si) and sodium aluminate (at a level of 1 mg/L Al) to synthetic sea-water to simulate the composition of interstitial pore water in the sea-bed sediments. It was expected that dissolution rates in this leachant would be even lower than in sea-water due to the higher initial concentrations of saturating species. Instead, it was consistently observed that the dissolution rates obtained in this leachant were at least as high as those obtained in deionized water. Furthermore, it was observed that the pH in the cases of other saline media (SW-Mg,Ca and SW-Mg) slightly increased during the leaching process due to the extraction of alkaline and alkaline earth components from the glass. In the cases of SW and POSW the pH remained nearly constant because of the low dissolution rates. (The exchange of K^+ for Ca^+ or of Ca^{2+} for Sr^{2+} should not affect the pH). On the other hand, a very significant decrease in pH was consistently observed upon leaching in SW+Si,Al.

Upon close inspection of the SW+Si,Al leachant it was observed that this solution was slightly turbid, unlike all the other leachants used in the present study. In order to identify the nature of the suspended material, a volume of 10 mL of SW+Si,Al was centrifuged and the supernate liquid decanted and

analyzed (see Table V). The precipitate was washed 3 times, each time with a few drops of a wash solution in order to remove the residual original liquid. Three wash media were used. The use of de-ionized water caused the precipitate to re-dissolve. The use of pure 2-propanol was observed to cause further precipitation from the residual aqueous solution. No visible change in the amount of precipitate was observed upon washing with a 1:1 2-propanol - water mixture. Accordingly, the precipitate washed with this mixture was re-dissolved in 10 mL of de-ionized water and analyzed. The results are recorded in Table V. A good materials balance was verified in the cases of Si and Al. (Mg, Na, Ca and K are present in the solution at very high concentrations.) It can be concluded that removal of the suspended solid results in a marked decrease in pH, and that the major components of the precipitate are Mg and Si, with small amounts of Na and Al present. The combined mole ratio of Mg and Na to Si is approximately 1:2. Accordingly, the solid is slightly basic (equilibrium pH of about 9.4), and its separation from the solution should cause a slight drop in pH. This is in agreement with the data in Table V.

The process of precipitation of a basic solid from the SW+Si,Al solution can be expected to be enhanced in the presence of the glass powder in the leaching experiment. The glass grains are likely to act as centers for precipitation and sorption of basic solid phases because of their large surface area and negative surface potential. Accordingly, while in the absence of

the glass the pH of the suspension is stable over a period of at least 6 months and no coagulation is observed, a substantial amount of basic salts can separate out when the glass is introduced. This would lead to a substantial decrease in pH, as shown in Tables III and IV. This mechanism is supported by the finding that the reaction of aqueous silica with sea-water produces a hydrated magnesium silicate similar to sepiolite³⁸⁻⁴⁰ and by the observation that this process,⁴⁰ as well as the aging of suspensions of various silicate minerals in sea-water,^{36,37} have been shown to result in a decrease in pH.

It is interesting to note that the leachates obtained in SW+Si,Al and even the leachant blanks are turbid following exposure to a temperature of 90°C for a period of 7-28 days. The solubility of sepiolite slightly increases with rising temperature. The activity product can be defined as $K_{sp}=[Mg^{2+}]^2 [H_4SiO_4]^3 \cdot [OH^-]^4$, and its value rises from $10^{-40.1}$ at 25°C to $10^{-37.2}$ at 90°C, corresponding to an increase by a factor of 9 in $[H_4SiO_4]$ if the other terms remain unchanged. However, for sea-water at pH 8.2 and 25°C the solubility of silica based on these data is only 30 μ Mole/L or 0.84 mg/L Si,³⁸ and increasing the temperature to 90°C should result in an increase in this value to 7.8 mg/L Si. This limiting value is much lower than the concentrations of Si in the leachant blanks (20 mg/L Si) and in the leachates (40 mg/L Si), and this can account for the turbidity observed in the solutions. The leachates are observed to be more turbid than the leachant blanks as a result of their

higher Si content and of the presence of dissolved Al. Consequently, the behavior of the system at 90°C appears to be in agreement with previous data for Mg silicate solubility. On the other hand, the concentration of Si in the centrifuged SW+Si,Al leachant stored at room temperature, 7.2 mg/L (see Table V), is much higher than the value expected on the basis of sepiolite solubility (0.84 mg/L Si, see above), and, as noted above, observed Si concentrations in interstitial pore water sampled at 2°C can reach 15-30 mg/L Si.²² This apparent discrepancy can be resolved by noting that at their low ambient temperatures both sea-water and interstitial water are supersaturated with respect to Mg silicates ^{22,38,39}, aluminosilicates ³⁸, and even pure quartz^{21,38}. The extent of supersaturation and solubility control by metastable species can be expected to be largest at low temperatures. Moreover, at these temperatures a significant fraction of Mg is bound in complexes such as MgSO₄.^{21,44}

The enhanced leaching of the microtektite glass in the SW+Si,Al solution (see Tables III and IV) can be attributed to the decrease in the pH of the solution as the basic solid separates out or, more directly, to the deposition of a wet basic layer on the glass surface. The decrease in the pH of the solution can result in a second-power rise in the solubility of the oxides of Mg, Fe, Ca and Sr, which account for 32% of the glass composition (see Table I). The large extent of glass dissolution at low pH is shown in Tables III and IV. On the other hand,

enhanced corrosion of silicate glasses when such glasses become covered with films of wet basic salts such as Na_2CO_3 is well-known in studies of atmospheric weathering.⁴⁶

The same mechanism may account for the finding that the dissolution rates of the microtektite glass composition in the synthetic sea-water leachant (SW) are somewhat higher than those observed in the case of actual Pacific Ocean sea-water (POSW, see Tables IV and V). The leaching process in SW, but not in POSW, results in a slight decrease in pH. The SW leachant initially contains more silica than POSW and therefore it may give rise to minor precipitation processes at 90°C which do not take place in POSW.

The experiments which indicated that basic silicate precipitation causes enhanced microtektite dissolution were carried out under conditions where introduced silica levels in synthetic leachants were high compared with the solubility level of silica or silicates in the system. Accordingly, it is not certain to which extent such a phenomenon affects the microtektite glasses in nature. As detailed in the previous section, calculations based on the results of leach tests in actual Pacific Ocean sea-water (which does not exhibit precipitation) agree very well with field observations on over-all microtektite corrosion. However, localized precipitation of basic species may account for the large extent of corrosion observed in the cases of some microtektites⁶ (up to 90 μm), and to the irregular corrosion patterns observed on the surfaces of microtektites⁴⁷ as well as land tektites.⁴

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TABLE I

Starting material	Oxide	Composition, wt. % oxide		
		undoped	doped	analyzed doped
SiO ₂	SiO ₂	50.4	49.8	47.5
MgCO ₃	MgO	21.2	21.0	21.1
Al ₂ O ₃	Al ₂ O ₃	16.8	16.7	17.4
Fe ₃ O ₄	FeO	6.5	6.4	6.9
CaCO ₃	CaO	3.7	1.8	2.1
TiO ₂	TiO ₂	0.8	0.8	0.8
Na ₂ CO ₃	Na ₂ O	0.4	0.4	0.4
K ₂ CO ₃	K ₂ O	0.2		0.1
SrCO ₃	SrO		2.3	2.2
Ca ₂ CO ₃	Ca ₂ O		0.3	0.1
H ₃ BO ₃	B ₂ O ₃		0.5	1.4

TABLE II

Composition of Leachants in Microtektite Studies, g/L

Leachant	NaCl	K ₂ SO ₄	CaSO ₄ .2H ₂ O	CaCO ₃	MgCl ₂ .6H ₂ O	MgSO ₄	MgBr ₂ .6H ₂ O	Na ₂ SiO ₃ .9H ₂ O	Na ₂ Al ₂ O ₄ .3H ₂ O	KH(COO) ₂ C ₆ H ₄
pH3										10.211
DIW ^a										
DIW+Si								0.506		
SW-Mg,Ca	40.462	0.863						0.030		
SW-Mg	37.517	0.863	1.593	0.123				0.030		
SW	27.213	0.863	1.593	0.123	8.129	1.658	0.121	0.030		
POS ^{wb}										
SW+Si,Al	27.213	0.863	1.593	0.123	8.129	1.658	0.121	0.202	0.003	

^aDe-ionized water^bPacific Ocean Sea-water(analyzed solute concentrations given as C° in Tables IV and V)

Table III
Leach Rates of Microtektites at 90°C, days 59-66

	Leachant	pH	Concentration ($\mu\text{g}\cdot\text{L}^{-1}$) and normalized leach rates ($\mu\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$)									
			Si	Mg	Al	Fe	Ca	Ti	Na	Sr	Cs	B
C ^o	pH3	3.10	0.05	0.01	0.03	0.06	0.06	0.00	0.32	0.01	0.11	0.00
C		3.26	98.4	44.3	12.7	7.05	8.27	0.04	2.63	12.2	1.39	0.63
L			203	168	69	67	307	4	365	307	251	192
C ^o	DIW	7.16	0.02	0.03	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00
C		9.02	14.1	2.01	1.55	0.01	0.90	0.00	0.41	1.23	0.36	0.17
L			29	7.5	8.4	0.1	33	0	65	31	71	52
C ^o	DIW+Si	7.83	36.7	0.02	0.00	0.02	0.15	0.00	63.1	0.01	0.04	0.01
C		8.43	39.7	0.19	0.95	0.08	0.38	0.00	63.1	0.21	0.07	0.03
L			6.2	0.6	5.2	0.5	8.9	0	1	5.2	7	5
C ^o	SW-Mg, Ca	8.61	3.72	0.20	0.04	0.04	2.02	0.00		0.16	0.00	0.19
C		8.89	8.94	2.23	2.65	0.16	2.59	0.01		0.89	0.07	0.23
L			11	7.7	14	1.2	21	1		18	14	12
C ^o	SW-Mg	8.38	3.49	0.01	0.20	0.42		0.01		0.33	0.00	0.32
C		8.41	7.97	2.16	1.99	0.45		0.01		1.12	0.04	0.37
L			9.3	8.2	9.8	0.3		0		20	8	15
C ^o	SW	8.14	0.71		0.10	0.51		0.01		0.36	0.01	0.20
C		8.11	1.40		0.14	0.54		0.01		1.29	0.09	0.25
L			1.4		0.2	0.3		0		23	16	15
C ^o	POSW	8.24	0.66		0.01	0.51		0.01		14.2	0.00	5.67
C		8.23	0.62		0.06	0.53		0.01		14.6	0.05	5.68
L			-0.08		0.3	0.2		0		10	10	3
C ^o	SW+Si, Al	8.21	16.9		0.73	0.49		0.01		0.36	0.05	0.68
C		7.54	44.2		4.66	1.26		0.07		7.11	0.51	1.02
L			56		21	7.4		6		170	90	104

Table IV
Leach Rates of Microtektites at 90°C, days 87-115

	Leachant	pH	Concentration (mg·L ⁻¹) and normalized leach rates (ng·m ⁻² ·d ⁻¹)									
			Si	Mg	Al	Fe	Ca	Ti	Na	Sr	Ce	B
C ^o	pH3	3.02	0.16	0.15	0.27	0.05	0.08	0.00	0.51	0.01	0.07	0.00
C		3.31	151	63.2	12.4	2.04	17.7	0.80	4.90	28.8	2.60	1.06
L			79	61	17	4.9	167	20	176	185	126	82
C ^o	DIW	7.24	0.02	0.01	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00
C		8.70	19.9	1.16	1.62	0.03	1.00	0.00	0.93	1.36	0.26	0.45
L			10	1.1	2.3	0.07	9.3	0	37	8.7	13	35
C ^o	DIW+Si	7.77	48.7	0.00	0.07	0.00	0.01	0.01		0.00		0.00
C		8.15	49.8	0.12	0.90	0.01	0.20	0.01		0.21		0.02
L			0.6	0.12	1.2	0.02	1.8	0		1.4		2
C ^o	SW-Mg,Ca	8.37	4.5	0.09	0.08	0.00	2.54	0.00		0.26	0.02	0.14
C		8.62	10.7	2.91	2.42	0.21	3.51	0.00		1.49	0.06	0.17
L			3.3	2.7	3.3	0.5	9.2	0		7.9	2	2
C ^o	SW-Mg	8.14	4.66	0.00	0.23	0.94		0.01		0.49	0.02	0.29
C		8.39	9.66	1.43	1.46	1.07		0.01		1.37	0.05	0.33
L			2.6	1.4	3.6	0.3		0		8.9	1	3
C ^o	SW	8.38	0.70		0.01	1.29		0.01		0.58	0.00	0.18
C		8.21	1.92		0.14	1.37		0.01		3.96	0.15	0.27
L			0.63		0.18	0.2		0		22	7.4	7
C ^o	POSW	8.46	0.87		0.14	1.34		0.01		15.3	0.00	5.33
C		8.46	0.60		0.18	1.42		0.01		17.4	0.03	5.36
L			-0.14		0.06	0.2		0		13	1	2
C ^o	SW+Si,Al	8.09	23.9		1.05	1.39		0.01		0.43	0.00	0.72
C		7.31	39.7		3.13	4.21		0.26		16.8	0.20	1.36
L			8.3		2.9	6.9		6		105	10	50

TABLE V

	pH	Concentrations, mg/L					Ca
		Si	Al	Mg	Na	K	
Original SW+Si,Al	7.58	16.3 \pm 0.7	2.0 \pm 0.2				
Centrifuged SW+Si,Al	7.22	7.2 \pm 0.3	1.6 \pm 0.2				
Re-dissolved residue ^a		8.8 \pm 0.4	0.46 \pm 0.06	2.4 \pm 0.2	1.06 \pm 0.03	0.16 \pm 0.01	0.10 \pm 0.01

^aObtained by centrifugation of 10 mL of original SW+Si,Al, rinsing in 1:1 2-propanol - water, and re-dissolution in 10 mL of de-ionized water.

LEGENDS TO FIGURES

FIGURE 1. Leach rates of the microtektite glass composition in synthetic sea water without Mg at 90°C (based on Si).

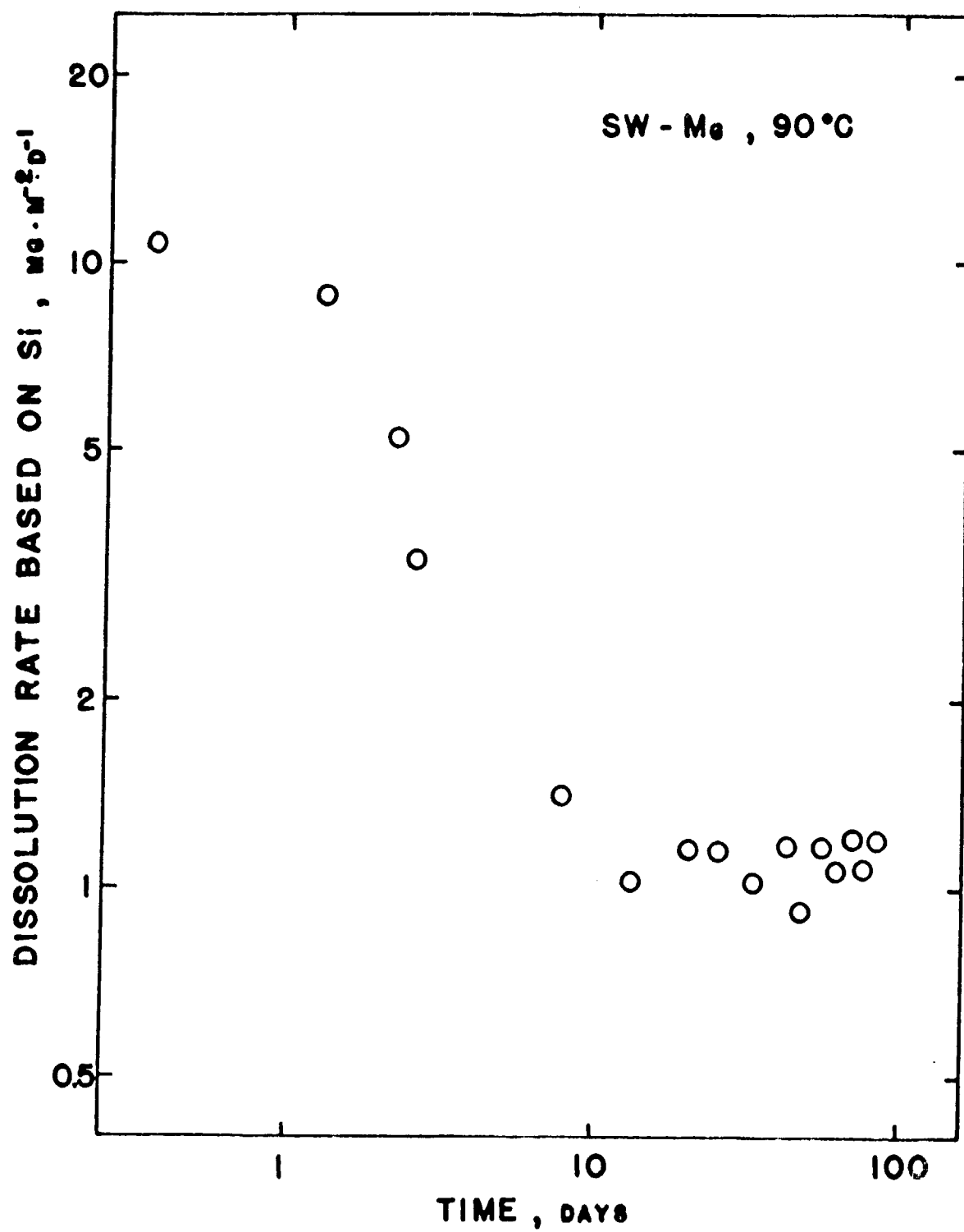


FIG.1